CLAIMS:

1. In a laser spray method for ionizing a liquid sample by irradiating, with a laser beam, the end of a capillary into which the sample has been introduced, an ionization method characterized by forming at least the end of the capillary of a substance that does not readily absorb the laser beam used.

2. An ionization method according to claim 1, wherein the laser beam is an infrared beam, and the substance that does not readily absorb the laser beam is any of diamond, silicon or germanium.

3. An ionization method according to claim 1 or 2, wherein a diamond tip provided with a small cavity for communicating with a slender cavity in an insulated capillary is attached to the end of the capillary.

4. An ionization method according to any one of claims 1 to 3, wherein at least the end of the capillary is placed in vacuum in the vicinity of an ion introduction port of a mass analyzer.

5. An ionization method according to any one of claims 1 to 3, wherein at least the end of the capillary is placed under atmospheric pressure in the vicinity of an ion introduction port of a mass analyzer.

6. An ionization method according to claim 1, wherein an electric field is formed in the vicinity of the end of the capillary by forming the capillary of an

electrical conductor and applying a high voltage to the capillary.

7. An ionization method according to claim 1, wherein the capillary is formed of an insulator, a conductive wire is placed inside the capillary and a high voltage is applied to the conductive wire.

8. An ionization method according to any one of claims 1 to 3, wherein at least the end of the capillary is placed in a corona-discharge gas, a corona-discharge electrode is provided in the vicinity of the end of the capillary and a positive or negative high voltage is applied to the corona-discharge electrode to thereby induce a corona discharge.

9. An ionization method according to claim 8, wherein the capillary is formed of an insulator, a conductive wire is placed inside the capillary and the end of the conductive wire is caused to project slightly beyond the end of the capillary to thereby serve as a corona-discharge electrode.

10. An ionization method according to claim 8 or 9, wherein the end of the capillary is placed in atmospheric pressure.

11. An ionization method according to any one of claims 8 to 10, wherein an assist gas be supplied to the vicinity of the end of the capillary.

12. An ionization method according to claim 11, wherein

an outer tube is provided on the outer side of the capillary with a clearance being left between itself and the outer peripheral surface of the capillary, and the assist gas is introduced to the vicinity of the end of the capillary through a space between the outer peripheral surface of the capillary and the outer tube.

13. An ionization method according to any one of claims 1 to 12, wherein irradiation is with a pulsed laser beam.

14. An ionization method according to any one of claims 1 to 12, wherein the liquid sample is passed through the capillary continuously and is irradiated with a laser beam that is generated continuously.

15. An ionization method according to any one of claims 1 to 14, wherein the end of the capillary is irradiated with the laser beam directed substantially along the axial direction of the capillary.

16. An ionization method according to any one of claims 1 to 14, wherein the end of the capillary is irradiated with the laser beam from a direction substantially perpendicular to the axial direction of the capillary.

17. In a laser spray apparatus for ionizing a liquid sample by irradiating, with a laser beam, the end of a capillary into which the sample has been introduced, an ionization apparatus characterized in that at least the end of the capillary is formed of a substance that does not readily absorb the laser beam used.

18. An ionization apparatus according to claim 17, wherein the capillary is formed of an insulating material, a diamond tip provided with a slender cavity that communicates with a slender cavity in the capillary is attached to the end of the capillary, and a conductive wire to which a high voltage is applied is placed inside the slender cavity of the capillary.

19. An ionization apparatus according to claim 17 or 18, wherein a corona-discharge electrode is provided in the vicinity of the end of the capillary.

20. An ionization apparatus according to claim 18, wherein the conductive wire is inside the capillary and extends to a point near the end of the capillary.

21. An ionization apparatus according to claim 18, wherein the end of the conductive wire is caused to project slightly beyond the diamond tip at the end of the capillary.

22. An ionization apparatus wherein an ionization space communicating with a mass analyzer through an ion introduction port is formed by a housing on the outer side of the ion introduction port of the mass analyzer;

at least the end of the capillary into which a liquid sample is introduced is placed inside the ionization space;

a laser device for irradiating the end of the capillary is placed outside the ionization space; and

at least the end of the capillary is formed of a substance that does not readily absorb the laser beam used.

23. In a MALDI method for ionizing a sample by irradiating the sample, which is mixed with and held by a matrix, with a laser beam, an ionizing method comprising:

using a low-molecular-weight inorganic matrix that includes water;

holding the sample, which has been mixed with the inorganic matrix, in a depression of a substrate formed to have a protrusion at least at a portion of the periphery of the depression; and

irradiating the sample with an infrared laser beam.

24. An ionization method according to claim 23, wherein an electric field is formed surrounding the sample held in the depression of the substrate.

25. An ionization method according to claim 24, wherein the electric field is formed by applying a high voltage to an electrically conductive substrate.

26. An ionization method according to any one of claims 23 to 25, wherein the substrate is porous silicon.

27. An ionization method according to any one of claims 23 to 25, wherein the substrate is cooled.

28. An ionization apparatus wherein an ionization space held in vacuum and communicating with a mass analyzer

through an ion introduction port is formed by a housing on the outer side of the ion introduction port of the mass analyzer;

a substrate having a depression at least a portion of the periphery of which is formed to have a protrusion is placed inside the ionization space; and

a laser device for irradiating a sample, which has been mixed with an inorganic matrix held in the depression of said substrate, with an infrared laser beam is placed outside the ionization space.

29. The ionization apparatus according to claim 28, provided with a cooling device for cooling said substrate.